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FULLERENE BASED NANOCOMPOSITES FOR ADVANCED OIL/GAS APPLICATIONS

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ABSTRACT

Fullerenes, novel forms of super carbonaceous materials are subject of significant research for their utilization in an increasing number of applications like petrochemical, energy, transportation, automotive, aerospace, defence, sporting goods and infrastructure development. In particular, carbon nanotubes and graphene are some of the common types of fullerenes that offer unique combinations of superlative chemical and physical properties. This keynote speech will look into how a simple chemical manipulation at nano-scale of a superlative chicken wire structure of graphene can be exploited to address major engineering challenges we are now encountering in the development of subsea engineering products used for oil/ gas applications. Substituting monolithic materials with nanofiller reinforced composites would not just bring major performance uplift but also significant reduction in manufacturing and related economics. However, there are several key challenges prior to this forthcoming substitution which will be detailed in this work.

Keywords: Graphene; alumina; fracture toughness; electrical conductivity; SPS.

1 INTRODUCTION

Advanced ceramics are having many applications in the very challenging oil and gas applications. As current reservoirs and other national resources of oil and gas are being depleted, the technology is being pushed to explore ever more severe and demanding environments for future supplies. New materials, like fullerenes, offer unique combination of extraordinary properties to such materials. Owing to the superlative nature of atomically thin graphene [1], its incorporation in ceramics has become a focal point for many ceramics researchers globally. For example, with the addition of just 1.5 vol% of graphene in silicon nitride, a remarkable 235% improvement in fracture toughness was achieved [2]. The graphene was found to be wrapped around the silicon nitride grains and formed a continuous network along the grain boundaries [2]. Kim et al. [3] reported an increase of one order of magnitude with the addition of only 0.25 vol% of graphene in alumina. Similarly, Zhou et al. [4] reported an increase of 8 orders of magnitude and 3.7 times in the electrical and thermal conductivity of ceramic-graphene nanocomposites respectively. The percolation threshold for the alumina – graphene nanocomposites was researched for the first time in 2010 [5], which was found to be around 3 vol.%. Fan et al. [5] reported increased electrical conductivity for the nanocomposites with increasing the amount of graphene, reaching a value of around 5710 S/m for alumina - 15 vol% graphene.

From the analysis of the literature studying ceramic – graphene nancomposites, it can be noted that majority of the research papers in the field of ceramic-graphene nanocomposites study the effect of the graphene content on the properties of the final ceramic – graphene nanocomposite [3]. In this study, we systematically report a novel and effective strategy for engineering the mechanical and electrical properties of ceramic – graphene nanocomposites without changing the amount of graphene.

2 EXPERIMENTAL DETAILS

Chopped graphene nanoribbons flakes were produced by the CVD pyrolysis of a solution containing ethanol, ferrocene and thiopene as reported in [6]. Freshly produced (raw) graphene was then aggressively tip-sonicated for 20-60 mins in distilled water using Z511463 Sigma-Aldrich ultrasonic tip-sonicator (750

W). The supernatant was collected and dried in an oven at 60 °C for 24 h prior to Raman spectroscopy. The Raman spectra for raw and damaged/ tip-sonicated graphene were obtained on a Renishaw Raman Imaging Microscope System. Sample masses ranged from 25 to 30 mg. Raman spectra were excited with a 488 nm Ar+ laser line at a power of 35 mW. Spectra were detected with an imaging photomultiplier (1024 x 1024) with 5 cm-1 resolutions. Typical collection time was 30 minutes for each sample and at least 5 batches of each sample were examined for accurate quantification of the ratios of the intensities for different bands (i.e. D, G and G'). Thermogravimetric analysis (TGA) was conducted for all nanocomposites to evaluate graphene oxidation temperature using TA Instruments SDT Q600. Q500 (TA instruments) was used with a heating rate of 5 °C/min to 1000 °C in air. All specimens were examined on platinum pans in the range 30–1000 °C. A heating rate of 5 °C/min in flowing air (at 180 ml/min) was used. Sample masses ranged from 40 to 50 mg and at least 3 samples were oxidised for each composition of selected nanocomposites.

For mechanical and electrical characterisations, alumina nanocomposites containing 0.5 vol% graphene (raw and damaged) were Spark Plasma Sintered (SPSed) respectively. Graphene nanopowder (chopped nanoribbons flakes produced by the CVD pyrolysis of a solution containing ethanol, ferrocene and thiopene as reported in [6] were dispersed in dimethylformadie, DMF [7] using high power tip ultrasonication for 45 minutes and then hand-mixed with alumina nanopowder (Sigma–Aldrich, UK: gamma phase; particle size <50 nm; surface area 35–43 m2 g−1; melting point 2040 °C; and density 3.97 g cm−3) for 10 min. The liquid mixture was rotation ball milled for 10 h. It was then dried at 70 °C for 12 h using a rotary drier containing milling media (4 mm alumina balls), followed by vacuum oven drying at 100 °C for 50 h. To avoid re-agglomeration of graphene during lengthy drying, the alumina balls (milling media) was added during rotary drying. The dried nanocomposite powder was ground and sieved at 150 mesh and then placed again in the vacuum oven at 100 °C for another 50 h to thoroughly extract the solvent. Nanocomposite pellets (diameter 20 mm and thickness 5 mm) were prepared by Spark Plasma Sintering (SPS) using LABOX 350 (Sinter Land Inc, Japan) furnace. A pressure of 100 MPa was applied concurrently with the heating (rate 60 °C min−1) and released at the end of the sintering period, which was 10 mins. Sintering temperature for all nanocomposites was 1250 °C. A pulsed DC current with 5 µsec ON and 5 µsec OFF was used without any pause.

All of the sintered samples were ground using SiC paper down to 4000 grit. The density of the ground samples was measured using the Archimedes' water buoyancy method and also verified by a manual Heliulm multipycnometre (Quantachrome UK). All samples were then thoroughly dried in an oven for 24 hours and then diamond polished using 1-micron paste. Sintered nanocomposite samples were gently fractured and their micro structures were examined in an FE-SEM. Cross-sectional surfaces were gold coated and observed in an ultra-high resolution analytical FE-SEM (Hitachi, SU-70) using 20 keV.

For mechanical and electrical characterisations, at least 5 samples of each composition were examined. Fracture toughness characterisations were carried out for alumina and nanocomposite samples according to standard ASTM C1421 (standard test method for determination of fracture toughness of advanced ceramics at ambient temperature). Single Edge V-notch Beam (SEVNB) method was employed using parallelepiped samples (3 x 4 x 30 mm2) and a loading span distance of around 17 mm. All samples were machined and notches were produced using a diamond saw (Accutom-50). For all samples, the notch was in the range of 0.7-1.1 mm in depth and around 195 µm in width. The root radius of the notch for each sample was about 9-10 µm with a V-notch angle of around 19o. For evaluating electrical conductivity, a bar (dimensions: 17 x 3 x 5 mm) was cut from each sintered pellet using precision and deformation-free cutting machine (Accutom-50). Around 500 microns of material was removed from all surfaces of sample by fine grinding. Four-point method [8] was employed by using a resistivity/ Hall measurement system (Quantum Design, PPMS, Model 6000) for measuring electrical conductivities of nanocomposites. For pure alumina samples, high resistance meter (HP 4329A) was used to measure the conductivity. The connecting wires in the experimental setup were permanently bonded by using silver paste in order to avoid any contact resistance for this analysis.

3 RESULTS AND DISCUSSION

Raman spectroscopy is a well-known and widely used characterisation technique for analysing carbon materials [9-15]. For graphene, the D-band near 1370 cm-1 and the D' shoulder band near 1630 cm-1 are, respectively, the disorder-induced features that are representing the intervalley K→K' and intervalley K (or K') double resonance scattering processes [9, 10]. G band, appearing at around 1620 cm-1, is associated with the doubly degenerate phonon mode at the Brillouin zone centre or tangential vibration of carbon atoms [9]. The sharpening of G band peak will shorten FWHM (Full Width at Half Maximum) line which confirms the establishment of larger crystalline areas [9, 11]. Similarly, the D band is the signature of defects and increase in ID/IG and ID/IG' corresponds to an increase in the amount of 'unorganised' carbon and/or decrease

in the mean crystal size as reported elsewhere [11-15]. During graphitisation, the ID becomes smaller than IG, which indicates a more perfect graphene structure [11, 13, 15]. Therefore, in this study, the authors used the ID/IG and ID/IG' ratios and FWHM line widths from Raman spectroscopy supported by electrical conductivity and oxidation temperature analyses to study the degradation of graphene after sintering.

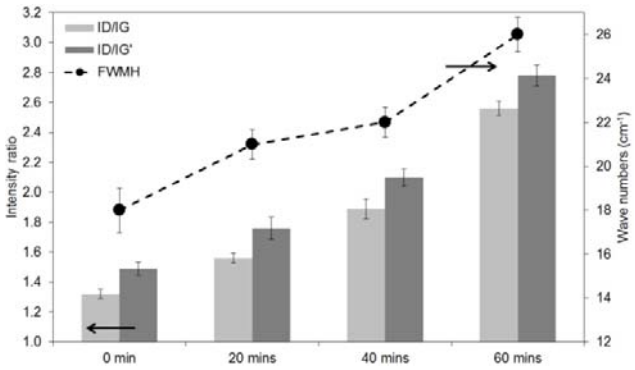

Figure 1. Raman spectroscopy analysis of as-produced and tip-ultrasonicated graphene showing intensity ratios and FWHM line widths (G band).

Figure 1 shows severe damaging of chicken wire structure in graphene due to severe ultrasonication. Qualitative information on purity, crystallinity and structural health of graphene was obtained from the Thermogravimetric analysis (TGA) of the sintered nanocomposites. Higher the content of oxidisable residue and amorphous carbon, lower the onset of oxidation temperature or thermal stability and vice versa [16, 17]. The crystallinity was also significantly reduced as confirmed from the TGA analyses as well (figure 2). Because of this damage, as confirmed via figures 1 and 2, fracture toughness and electrical properties were also found to be severely affected (figure 3). It can be seen that with the increase in the damage or the amorphous content within graphene, lower fracture toughness and electrical conductivities were observed.

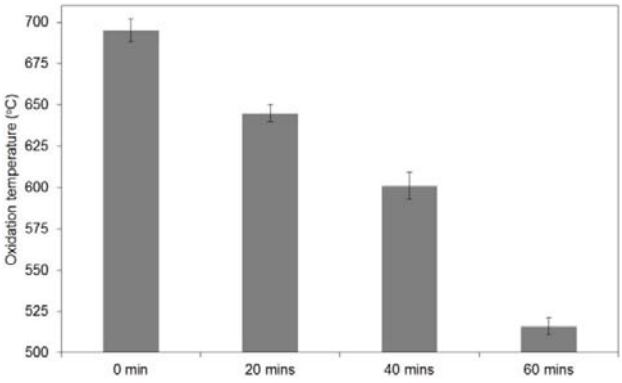

Figure 2. Thermogravimetric analysis (TGA) of as-produced and tip-ultrasonicated graphene.

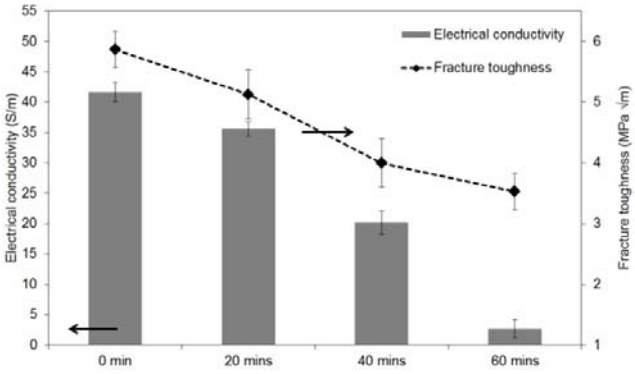

Figure 3. Electrical conductivity and fracture toughness values of the nanocomposites measured by four-probe and Single Edge V-notch Beam (SEVNB) techniques respectively. For electrical and mechanical characterisations, alumina nanocomposites containing 0.5 vol% graphene (raw and damaged) were sintered respectively.

Fig 4 shows the FE-SEM images of fractured surfaces of the representative sintered nanocomposite samples (i.e. alumina – 0.5 vol% graphene). Individual layers of graphene are pointed and found crushed between alumina grains. Good dispersion of graphene in the alumina matrix can be observed (fig 4). Individual grains and intergranular fracture mode along with pulled out graphene from the alumina grains can be visualised. With the addition of carbon nanofillers in ceramics, finer microstructures are produced as previously reported [18, 19]. For example, Wang et al. [18] observed that the addition of 2 wt% graphene in the alumina matrix resulted in grain size refinement. The grain size of pure alumina was 1 μm, while the grain size of composites was around 500 nm [18]. From the analysis of figure 4, no structural or grain size differences can be observed. Therefore, it can be concluded that the quality of graphene has no influence on the grain size refinement.

For enhancing electrical or mechanical properties of alumina nanocomposites, researchers have always added more graphene and proposed new effective dispersion strategies. Such enhanced properties can only be achieved if graphene is thoroughly homogenised/ dispersed, i.e. having maximum surface area in contact with the ceramic grains. There is always a limit for adding graphene in ceramic nanocomposites because higher the concentration of graphene, the more difficult it becomes to homogenise. As we mix more and more graphene with ceramic powder in a liquid solvent, the viscosity of the solution increases. Therefore, new experimental variables (related to dispersion) are required if different amounts of graphene are mixed with ceramic powder. With this new method, there is no need to optimise experimental variables related to dispersion prior to the wet processing for homogenisation, because we can customise the properties of final composite

material by changing the quality of incorporated graphene.

4 CONCLUSION

A novel strategy for producing ceramic – graphene nanocomposites with customisable mechanical and electrical properties without changing the amount of graphene has been presented. Structural and crystalline defects were produced in graphene using high-power tip ultrasonication for 20, 40 and 60 minutes. Raman spectroscopy and thermogravimetric analyses were conducted to characterise degradation in graphene. Alumina – graphene nanocomposites were then prepared using Spark Plasma Sintering. Fracture toughness and electrical conductivities were measured for alumina nanocomposites containing 0.5 vol% graphene respectively. Electrical conductivity and fracture toughness values of alumina – graphene nanocomposites decreased with the increase in structural defects in graphene. The quality of graphene has no influence on the grain size of the alumina nanocomposites.

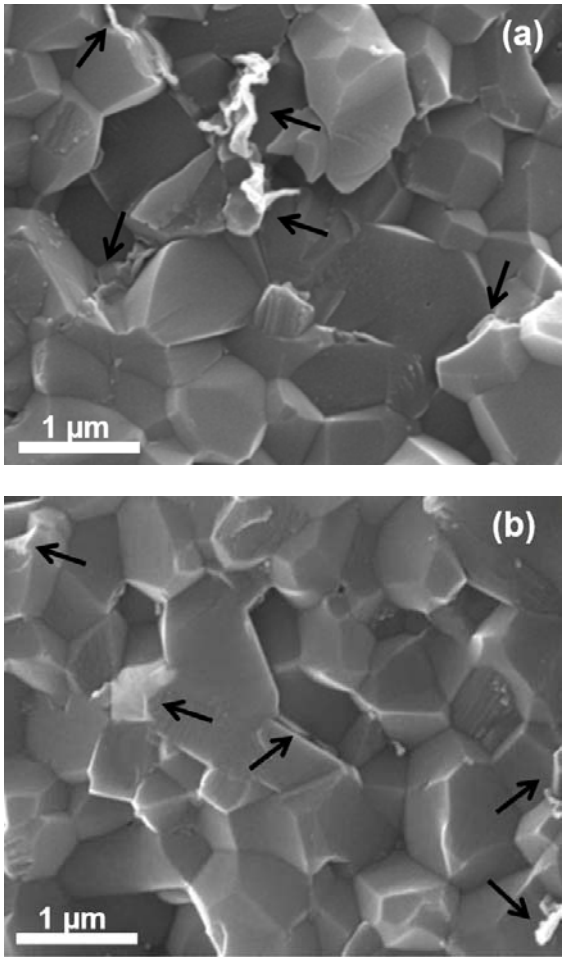

Figure 4. Representative FE-SEM images showing alumina – 0.5 vol% graphene nanocomposite having graphene tip-ultrasonicated for: a) 0 minute (as produced); and b) 60 minutes.

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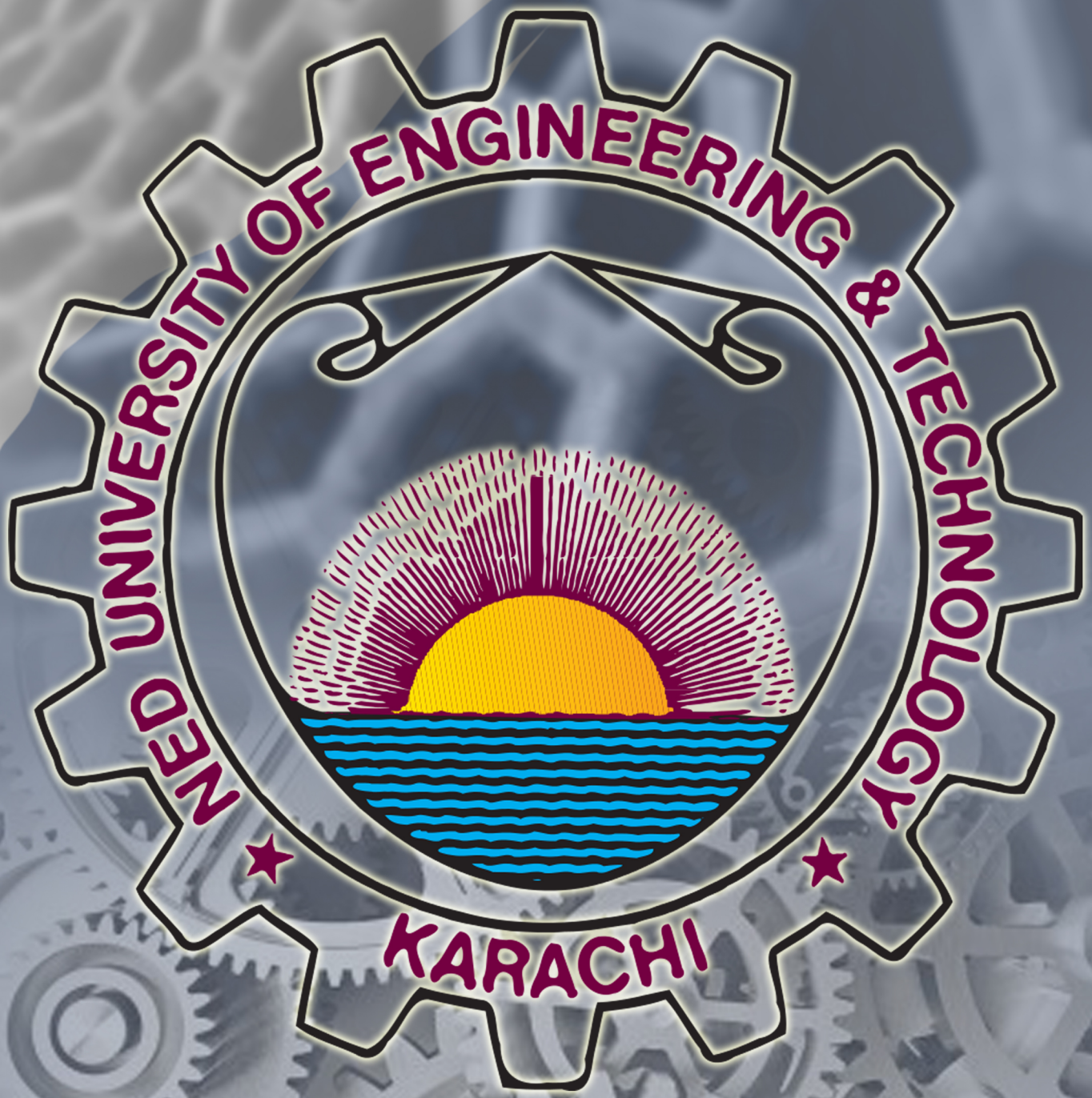

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